

Title: Effect of Boiler Operations on Sulfuric Acid Emissions
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Summary

Abstract

Sulfur trioxide is formed in the furnace and convective pass of coal- and oil-fired boilers; and the rate of formation depends strongly on boiler design and operating conditions. The SO_3 leaves a typical coal-fired utility boiler as a liquid deposit trapped on the air preheater baskets, as SO_3 and H_2SO_4 vapors adsorbed onto fly ash, and as H_2SO_4 vapor carried out the stack. The design and cold end operating conditions of the air preheater govern the fraction of SO_3 which flows from the air preheater with the flue gas. Rates of adsorption onto fly ash downstream of the air preheater are a complex function of ash surface properties and gas composition and temperature. This paper reviews a series of laboratory, theoretical and field investigations carried out at the Energy Research Center on the fate of SO_3 and H_2SO_4 in coal-fired boilers.

Introduction

Small quantities of sulfur trioxide (SO_3) are present in the flue gas from coal-fired boilers. The SO_3 has a beneficial effect of reducing the resistivity of fly ash and promoting its capture in cold side electrostatic precipitators. However, there are also undesirable impacts of SO_3 , including corrosion and fouling of heat exchangers, corrosion of duct work and formation of acid mist in the stack plume. The extent to which SO_3 affects emissions and contributes to equipment maintenance problems is influenced strongly by the design of the boiler, fuel properties and the operating conditions of the boiler. To understand how these elements fit together, it is necessary to first examine the processes by which SO_3 and sulfuric acid are formed.

SO_3 Formation

Figure 1 shows a sketch of a typical pulverized coal boiler. The coal is burned in the furnace and the product gases then flow from the furnace, through a series of heat exchangers in the convective pass, to the economizer gas exit duct. The gas temperature ranges from 2000 to 2500°F at the furnace exit to

600 to 700°F at the economizer gas exit. The gas temperature then decreases through the air preheater to about 300°F at the air preheater exit. For units with cold side electrostatic precipitators, the flue gas flows from there to the ESP inlet before going up the stack.

The SO_3 is formed by the reaction of sulfur dioxide (SO_2) with atomic oxygen (O) in the furnace and by the catalytic oxidation of SO_2 with molecular oxygen (O_2) in the convective pass region of the boiler. There are numerous design and operating parameters which influence the degree of SO_3 formation. Among these are fuel sulfur content, ash content and composition, convective pass surface area, gas and tube surface temperature distributions, excess air level, and coal fineness. Thus, the same fuel burned in two different boilers, or, in the same boiler at two different operating conditions, can produce substantially different levels of SO_3 . This is illustrated in Table 1 which shows concentrations of SO_3 measured in the economizer gas exit duct at three different boilers. All three boilers are of pulverized coal design and burned eastern bituminous coals with typical sulfur contents of two to three percent.

Processes within the Air Preheater

Virtually all utility boilers use air preheaters to transfer energy from the hot gases leaving the economizer to the air flowing into the boiler. Two types of air preheaters are in common use, the rotary regenerative type and the tubular type, with the regenerative design capturing the largest share of the utility market. Very typically, the gas temperature is reduced within the air preheater from an inlet level of 600-700°F to an exit level of about 300°F. During this process, the SO_3 undergoes some important changes. Gas phase SO_3 reacts with vapor phase H_2O to form vapor phase H_2SO_4 . The extent of this reaction depends on temperature and the reaction is essentially complete by the time the flue gas has reached the cold end of the air preheater. Condensation of H_2SO_4 and H_2O subsequently occur if the local metal temperatures in the air preheater flow passages drop below the acid dewpoint. Dewpoint is a function of both H_2O and H_2SO_4 concentrations in the flue gas, generally ranging from 250 to 285°F.

At metal temperatures below the acid dewpoint, the rate of condensation of sulfuric acid on the surface is strongly dependent on the acid concentration of the flue gas and wall temperature. In addition, in a rotary regenerative air preheater, where the flow passages are alternately exposed to combustion air and flue gas, evaporation of condensed acid occurs from the surface of the flow passage to the incoming air stream. The extent to which this evaporation process occurs is primarily a function of the moisture content of the inlet air and the surface temperature of the flow passage.

Due to the design of the air preheater and its mode of operation, there are strong transverse variations in gas temperature and H_2SO_4 vapor concentration leaving the air preheater. Thus, due to condensation within the air preheater, the average $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration of the gas flowing through the air preheater can easily be decreased by a factor of 2. At the same time, it is not unusual to see extremely large variations in $\text{SO}_3/\text{H}_2\text{SO}_4$ vapor concentration from one side of the gas exit duct to the other.

Fly Ash Adsorption

In addition to condensing onto cold metal surfaces in the air preheater and at the duct walls, H_2O and SO_3 become adsorbed onto the surface of the fly ash particles entrained with the flue gas. The rate of adsorption increases rapidly as the flue gas reaches the cold end of the air preheater, and this process continues as the flue gas flows through the duct connecting the air preheater to the electrostatic precipitator. Recent studies at the ERC show the rate of adsorption to depend strongly on temperature, gas phase SO_3 and H_2O concentrations and ash surface properties. The adsorbed acid and water have a large effect on fly ash resistivity and thus control ESP performance. In some units, additional SO_3 is injected into the flue gas to condition the fly ash and improve ESP collection efficiency.

Interaction with Ammonia

Use of NH_3 for fly ash conditioning or for NO_x control using SNCR or SCR technology is complicated by the presence of SO_3 . Ammonia and SO_3 react at temperatures higher than the typical acid dewpoint to form ammonium sulfate and bisulfate deposits. This has caused severe maintenance problems in some units due to accelerated rates of corrosion and heat exchanger fouling.

Conclusions

Having SO_3 in flue gas is an unavoidable consequence of burning fuels containing sulfur. The SO_3 is both a help and hindrance. It plays an important role in promoting high ESP collection efficiencies, but it also causes maintenance problems and it impacts on power plant efficiency. Efforts to optimize boiler operations to reduce emissions and minimize the cost of generation should consider the impacts of SO_3 on the boiler.

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Table 1: Measured SO₃ Concentrations in Economizer Gas Exit Ducts

Pulverized Coal Fired; 2 - 3% Sulfur Coal			
Unit	SO₃ (ppm)	Unit Load (MW)	O₂ (%) at Economizer Gas Exit
A	1 - 2.5	585	2 - 4
A	2.5 - 5	425 & 300	4 - 7
B	20	640	--
C	21 - 24	700	4 - 5
C	27	180	10

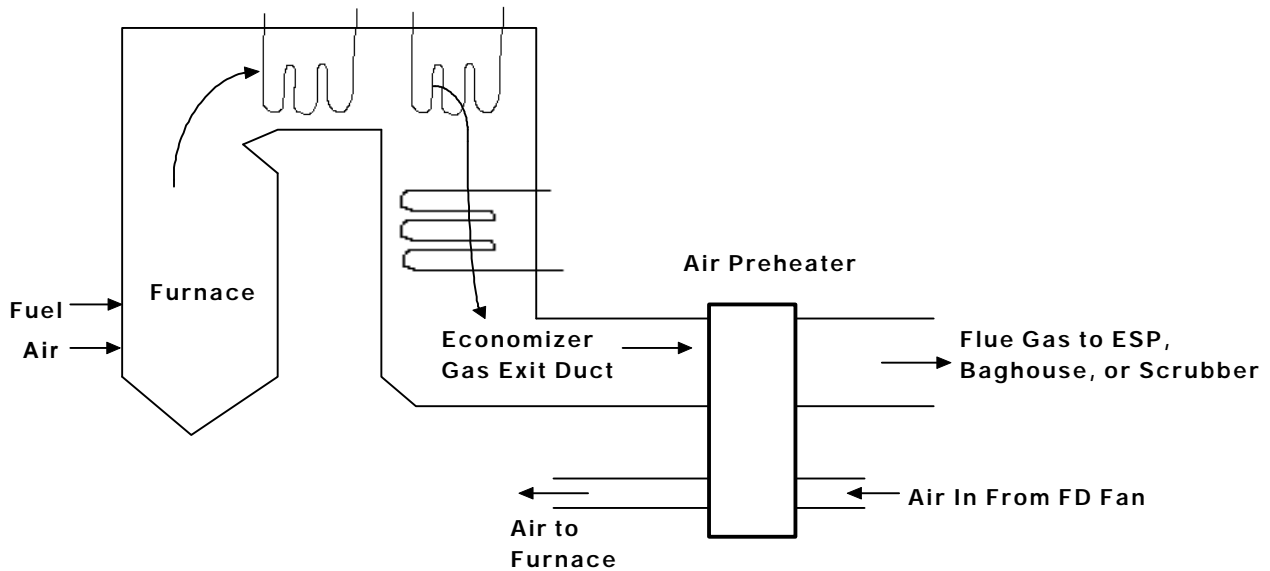


Figure 1: Sketch of Typical Pulverized Coal Boiler